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Experimental and DFT studies of structure, optical and magnetic properties of $(Zn_{1-2x}Ce_xCo_x)O$ nanopowders

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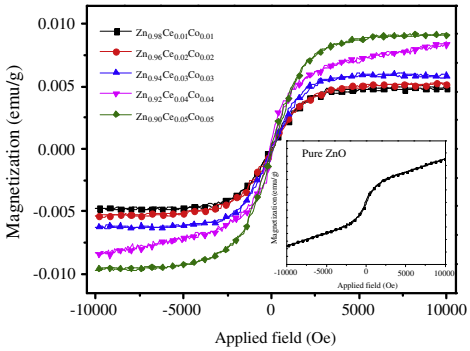
HIGHLIGHTS

- Ce, Co co doped ZnO nanoparticles are produced using a microwave combustion route.
- As synthesized nanoparticles have the wurtzite structure.
- Morphological investigation revealed the nanoparticles in the range of 25–60 nm.
- DRS measurements showed decrease in the energy gap with increasing dopants content.
- DFT indicates Ce governs stability, while Co adjusts the magnetic characteristics.

GRAPHICAL ABSTRACT

Microwave-assisted combustion method was used to develop the nanophase powders. The shift in the XRD peak position, changes in peak intensity, cell parameters, and cell volume confirms the substitution of Ce and Co into ZnO lattice. SEM images show that the average crystal size decreased from 50 nm to 25 nm when co doping concentration was increased. The vibrating sample magnetometer (VSM) revealed that the doped samples exhibited ferromagnetism at room temperature. Using first principles calculations, we predicted the magnetic and electronic properties of co-doped ZnO for different dopants concentration.



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ABSTRACT

A simple one-step microwave-assisted combustion method using urea as a fuel, was applied to develop the nanophase powders of $((Zn_{1-2x}Ce_xCo_x)$ O ($x = 0.00$, 0.01, 0.02, 0.03, 0.04, and 0.05)). The results emphasize that by changing the codopant concentration it is feasible to fine-tune structural, morphological, optical and magnetic properties. The synthesized nanoparticles gave rise to new microstructures without changing the basic hexagonal wurtzite structure. The substitution of Ce and Co into ZnO lattice was confirmed from the shift in XRD peaks position, changes in peaks intensity, and cell parameters. Energy dispersive X-ray spectra confirmed the presence of Ce and Co within ZnO system; the weight percentage was close to their nominal stoichiometry. Ultraviolet–visible (UV–Vis) spectroscopy analysis indicated that the optical band gap decreased with the increase of Ce and Co codoping concentration. It is clear from SEM images that the average particles size decreased from 50 nm to 25 nm when codoping concentration was increased up to 0.05 M. Photoluminescence spectra exhibited the emission bands in ultra-violet and blue–green regions. Magnetization-Field (M–H) hysteresis loops revealed that the

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codoped nanopowders exhibited room temperature ferromagnetism (RTFM). Using first principles calculations, based on density functional theory, electronic and magnetic properties of codoped ZnO for different dopants concentration, were predicted. It is found that the observed RTFM is originated mainly from spin polarization of Co-d orbital, Ce-f orbital has partial contribution.

Introduction

Research in manufacturing nanosized semiconductors is a field at the limelight of nanotechnology, because of its wide range of applications in nano-electronics, photonics, data storage, and sensing. The tenacious passion on these materials emanate from the enthusiasm in designing and building structures that display the dominant electrical, mechanical, chemical, optical and magnetic properties than the bulk materials. Due to the unique characteristics and size effects, nanomaterials often exhibit unusual physical properties from their bulk counterparts [1].

ZnO with wurtzite crystal structure is a encouraging semiconductor material in the field of ultraviolet (UV) light-emitting diodes, laser diodes, photo detectors, and thin film transistors in view of its wide direct band gap (Eg ~ 3.37 eV) and high exciton binding energy (60 meV) at room temperature [2]. The exclusive properties of ZnO makes it available for many applications, which also includes the production of paint and ceramics [3], photocatalyst [4], electronics [5], transistor [6], optical device [7], dye-sensitized solar cell [8], and solid-state gas sensor [9]. Besides, the technological significance of ZnO nanostructures, their quasi-one-dimensional structure with diameters in the range 10–100 nm, attracted significant interest in scientific point of view. To fine-tune the structural, optical, magnetic and other properties of ZnO nanostructures, it is efficient to dope or decorate ZnO with other elements. Owing to its wide energy band gap, ZnO can be used as a potential host lattice for doping several rare earth and transition metal ions. Consequently, it performs as an important host material for several applications.

Among the single-doped ZnO, Ce-doped ZnO nanoparticles have captivated most of the researchers mind for their considerable advantages in terms of excellent optical and photocatalytic properties, and an improved electrical conductivity [10–12]. However, Co-doped ZnO nanoparticles were reported for their improved ferromagnetism at room temperature and enhancement of both electrical conductivity and photoluminescence [13,14]. Furthermore, Zn can be easily substituted by Co ions without creating a large lattice distortion, due to their relatively equal ionic radius (Zn is 0.074 nm and Co is 0.072 nm). Reliable reports related to Co and X (N, Al, Fe, Ni) co-doped ZnO nanoparticles, such as Co–N co-doped ZnO thin films showed higher magnetic moment than Co single-doped ZnO [15]. Co–Al co-doped ZnO nanoparticles demonstrated increased ferromagnetism [16] and Co–Fe co-doped ZnO nanoparticles exhibited comparably high coercivity than the undoped [17]. First-principles calculations performed by Zhang et al. [18] showed the stabilization of ferromagnetism in $Zn_{1-x}Co_xO$ when co-doped with Al. Based on DFT calculations, Assadi et al. [19] have predicted ferromagnetism in hole mediated (Co, N) co-doped ZnO thin films.

Accordingly, it is evident that Ce and Co co-doped ZnO can be inviting because it will enrich some of the properties of ZnO nanoparticles (optical and magnetic), without destabilizing the original wurtzite crystal structure. It follows that the study of co-doping of TM metal with non-magnetic elements will contribute to interesting results.

Various chemical methods such as sol–gel [20], precipitation/coprecipitation [21,22], hydrothermal [23], microemulsion [24], pyrosol [25], and electrochemical methods [26] have been utilized to attain nanostructured doped ZnO nanoparticles. However, these methods are characterized by complex processes, expensive precursors and low production rates. On the other side, microwave-assisted path for the synthesis of nanomaterials is one of the promising techniques. The major advantages of this method are uniform heating, energy conversion at the reaction sites, producing small particle size metal oxides with high purity, selective formation of specific morphology, reduced energy consumption, and higher product yields [27,28]. Additionally, organic compounds (e.g. glycine, urea, citric acid, alanine and carbohydrazide) are used as fuel to enhance the efficiency of combustion synthesis. Among them, urea is cheap and readily available commercially and non-carcinogenic. When urea is employed as fuel together with nitrate salt of a cation and heated at 400 °C, the exothermic reaction between nitrates (oxidant reactant) and urea (fuel) leads to the creation of the corresponding nanocrystalline oxides. The primary benefit is that the required heat for synthesis is derived directly from the reaction [29,30], in which the metal nitrates operate both as oxidants and as cation sources, while the organic compound behave as fuel.

The aim of this study is the enhancement of luminescence and magnetic properties of ZnO nanoparticles by codoping with dual impurities (i.e. one is nonmagnetic (Ce) and other is diamagnetic material (Co)). The main challenge for this kind of materials is to attain ferromagnetic character at room temperature in order to be profitable for technological applications. Thus, the effects of reducing size as well as codoping (Ce, Co) of ZnO nanoparticles, are investigated in order to determine their influence on the morphology, luminescence and ferromagnetic properties. To the best knowledge of the authors, there is no report on the preparation and characterization of microwave combustion method using urea as fuel for codoped ZnO nanostructures. In this paper, undoped

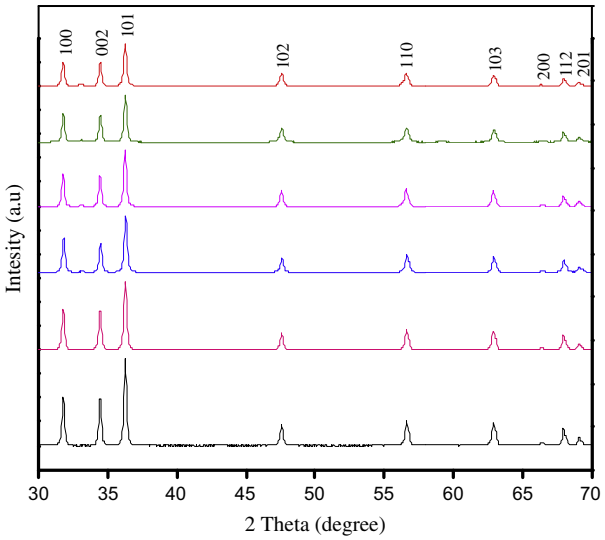

Fig. 1. (a–f) XRD patterns of (a) pure ZnO, (b) $Zn_{0.98}Ce_{0.01}Co_{0.01}O$, (c) $Zn_{0.96}Ce_{0.02}Co_{0.02}O$, (d) $Zn_{0.94}Ce_{0.03}Co_{0.03}O$, (e) $Zn_{0.92}Ce_{0.04}Co_{0.04}O$, and (f) $Zn_{0.90}Ce_{0.05}Co_{0.05}O$ samples.